

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

(logo)

European Patent Office

Publication No. **0 309 337**
A1**EUROPEAN PATENT APPLICATION**

Application no. 88 402 371.4

Int. Cl.: C 08 K 3/08
C 08 L 27/12, C 08 J 5/22

Date of filing: 9/20/88

Priority: Sept 25, 1987 FR 8713205

Date of publication of application:
March 29, 1990 Bulletin 89/13Designated Contracting States:
AT BE CH DE ES FR GB GR IT LI LU NL SEApplicant: ATOCHEM
4 & 6, Cours Michelet La Defense 10
F-92800 Puteaux (FR)Inventor: Platzner, Olivier
78 Avenue de Paris
F-92320 Châtillon (FR)Amblard, Jean
2 Allée Georges Rouault
F-75020 Paris (FR)Bolloni, Jacqueline
14 Boulevard Palaiseau
F-92190 Meudon (FR)Marignier, Jean-Louis
3 Rue des Terres-Nouvelles
F-92190 Meudon (FR)

Ion exchanger fluoropolymers containing metallic aggregates in the resin or at the surface, and a process for producing them.

The invention is related to a composition comprising metallic aggregates and at least one ion exchanger fluoropolymer, and particularly in the form of membranes charged with aggregates in the resin and that can be dressed with several layers of polymer that contain aggregates. These products are obtained by irradiation of membranes or fluoropolymer in a solution containing the metallic ions that are to be reduced.

EP 0 309 337 A1

Description

ION EXCHANGER FLUOROPOLYMERS CONTAINING METALLIC AGGREGATES IN THE RESIN OR AT THE SURFACE, AND A PROCESS FOR THE PRODUCTION THEREOF.

5 The present invention concerns ion exchanger fluoropolymers containing metallic or multimetallic aggregates in the mass or resin [instead of resin, the French original document throughout the text uses a more generic word, maybe, namely mass. (T.R.) = Translator's Remark(s)] or at the surface, and a process for making them. This process consists in a radiolytic reduction of metallic salts.

10 These products are useful as solid electrolytes or as membranes for the separation of gases.

15 The U.S. patent No. 4,629,709 describes aggregates of non-noble metals in colloidal solutions that contain polyvinyl alcohol.

20 A new composition has now been found comprising metallic or multimetallic aggregates and at least one fluoropolymer. The ion exchanger fluoropolymer preferably contains groups of sulfonic or carboxylic acids; this is for instance a product of the polymerization of a perfluorvinyl ether containing groups of sulfonic or carboxylic acids, or of the copolymerization of this ether with any copolymerizable product, for example styrene or divinyl benzene.

25 The metallic or multimetallic aggregates are small particles of metal, for example of dimensions in the order of one nanometer to one hundredth of a nanometer.

30 Advantageously, the aggregates of the present invention have an average diameter smaller than 50 nm, and preferably between 0.6 and 10 nm. The aggregates of the invention may be of the mono-dispersed type.

35 The aggregates may be composed of one or several metals. It can be one or several noble metals, or one or several non-noble metals and one or several non-noble metals, or one or several non-noble metals.

40 The aggregates may also be a mixture of aggregates of one metal 1 and of aggregates of one metal 2. These two populations of aggregates can be monodispersed. Metal 1 and metal 2 may each be a mixture of one or several metals as defined above. This means that it is possible to have aggregates of one metal or of one alloy and aggregates of another metal or of another alloy in one ion exchanger fluoropolymer. It is possible without departing from the scope of the invention described and claimed herein to have a mixture of aggregates of a metal 1, metal 2 ... metal n; each one of the metals 1, 2 ... n being defined as above.

45 By noble metal is meant any metal whose redox potential is positive: for example gold, iridium, platinum, rhodium, ruthenium, palladium, mercury, silver, osmium, copper... The non-noble metal is therefore the one which does not meet the preceding criterium, and examples thereof are nickel, cobalt, iron, zinc, antimony, tin, bismuth, lead, thallium ...

EP 0 309 337 A1

5 The composition according to the invention may present itself in the form of a colloidal solution or in the solid form such as a membrane. The colloidal solution is in the form of a dispersion of aggregates in the ion exchanger fluoropolymer in the presence of a solvent. This solvent can be any suitable solvent among these fluoropolymers, for example the dimethylformamide (DMF), or a mixture of water and alcohol. The alcohol employed is preferably an aliphatic alcohol having 1 - 5 carbon atoms.

10 The membrane may be for instance the one that is used in the cells for electrolysis of NaCl to produce chlorine in a process named "à la membrane".

The thickness of the membrane may be optional but preferably it should be between 0.05 and 1 mm.

15 The compositions according to the invention are in the form of metallic or multimetallic aggregates located in the resin of the membrane or at its surface, or both in the resin and at the surface. The choice could also be to have the charge in metal and the size distribution of the aggregates at a certain depth. These distributions can also be of the monodispersed type. According to one particular form of the invention, the diameter of the aggregates diminishes as their location extends depthwise.

20 As for aggregates in the resin of the membrane or dispersed in the colloidal solution, their quantity is ordinarily less than 20% by weight of the ion exchanger fluoropolymer and preferably between 0.001 and 10% by weight of the ion exchanger fluoropolymer.

25 The metal or metals of the aggregates on the membrane surface may be different from those of aggregates contained in the membrane. The compositions according to the invention may also include different successive layers of ion exchanger fluoropolymer containing metallic or multimetallic aggregates deposited on the membrane. These layers may be on one or the other of the two membrane faces, and the metal or metals of aggregates of various layers may be different.

30 The total quantity of metal at the membrane surface or contained in the different layers of fluoropolymer adhering to the membrane is ordinarily lower than 20mg/cm² of membrane and preferably ranging between 0.001 and 10 mg/cm².

35 The present invention also concerns a process for preparing the above described compositions.

40 This process is characterized in that a solution of at least one metallic salt is brought into contact with the ion exchanger fluoropolymer, and then by implementing a radiolytic reduction of the metallic salt or salts.

45 It is sufficient to select one salt of the metal (or metals), the aggregates of which are to be obtained, and then to put them in contact with the fluoropolymer. The radiolytic reduction occurs through irradiation with the aid of ionizing radiation, for instance through irradiation by means of x-rays or gamma-rays, or even accelerated particles.

EP 0 309 337 A1

Compositions in colloidal form are made active, and a solution of salt or salts or metallics to be reduced and of fluoropolymer is prepared, for instance by dissolving the fluoropolymer in a water/alcohol mixture and by adding thereto the metallic ions to be reduced. Advantageously, an aliphatic alcohol is used and preferably an alcohol that has 1 - 5 carbon atoms. The alcohol can be replaced by another polar solvent, for example the dimethylformamide.

Ammonia in solution may be added to facilitate the solubilization and stabilization of the metallic salts, specifically in the case of ammoniated complexes such as $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ or $\text{Ni}(\text{NH}_3)_6\text{SO}_4$.

The radiolytic yield can be increased by adding a transducer of radicals (OH , H ...) into the solution. This transducer is preferably a formate of the metal itself, a formate of alkaline metal, a formate of ammonium, or an alcohol.

The solution concentration of the metallic ions to be reduced is advantageously lower than 10^{-1} and preferably between 10^{-4} and 5×10^{-3} moles per liter. The concentration of ion exchanger fluoropolymers in this solution is advantageously lower than 30% by weight and preferably between 0.1 and 10%.

The solution containing the fluoropolymer and the metallic ions to be reduced is advantageously de-aired before irradiation, for example by splashing or spraying [purging?? (T.R.)] with nitrogen, argon or by applying a vacuum. The pH of this solution is adjusted, between the values limiting the solubility of the metal salts. In the case of non-noble metals the pH is preferably higher than 7.

The radiolytic reduction yield is progressively improved the higher the pH. It can be adjusted, from case to case, with a hydroxide of an alkaline metal or with dissolved ammonia.

Upon activating the compositions in their membrane form, pre-cleaning of the membrane is advantageously carried out.

The membrane is for example degreased with a suitable solvent (F 113), then boiled in a water/ethanol mixture with the aim to eliminate impurities. (F113 denotes trichlorotrifluoroethane.) The membrane can be exchanged, in the form of Na^+ by wetting (approx. 16 hours) in a NaOH 20 g/l solution, or in the form of NH_4^+ by wetting in a concentrated solution of ammonia to eliminate its acidity if any.

The membrane is impregnated with metallic ions by immersion in the a solution containing one or several salts of the metallic ion or ions to be reduced.

The solvent of the solution is a solvent or mixture of suitable solvents allowing the dissolving of the metallic salt or salts as well as bulging of the membrane. It is generally a mixture of water and alcohol (from 100:0 to 0:100% in volume) which allows for the control of the bulging of the membrane. The alcohol can be substituted by another suitable solvent. Advantageously, an aliphatic alcohol is used and preferably an alcohol that has 1 - 5 carbon atoms.

EP O 309 337 A1

Dissolved ammonia may be added to facilitate the solubilization and stabilization of the metallic salts, specifically in the case of ammoniated complexes ($\text{Ni}(\text{NH}_3)_6\text{SO}_4$, $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$).

Before immersion into the solution of metallic salts, the membrane may be wetted in a solvent that can be the same as the solution of metallic ions. In that way the bulging of the membrane is adjusted. If the membrane is of the cation type, from selecting a solution of metallic cations, their migration inwardly is favored and during the radiolytic reduction there is preferably obtained a deposit or sediment in the resin and at the surface. If a solution of anions is selected, a deposit at the surface and in the superficial layers of the membrane is favored. In addition the bulging is substantial and the achieved depth is great. For the anion membranes the procedure is the same but with inverted charges.

The higher the temperature is during this immersion, the more the membrane will bulge and may favor the migration into the resin of the metallic ions to be reduced.

Extensive bulging of the membrane may also facilitate the production of bulky aggregates.

The concentration of metallic ions in the solution may attain all values. It is only restricted by the limit of solubility of the metallic salts used in the solvent employed. It is preferably in the range of 5×10^{-4} and 5×10^{-1} moles/liter.

The pH of the solution is between the values of pH limiting the solubility of the metallic salt or salts used. It can be adjusted so as to control the ion exchange between the membrane and the solution.

The impregnation temperature may vary between the solvent's fusion and boiling points. Not in any case does the temperature reach the temperature of decomposition of the membrane.

The duration of impregnation may vary between 0 and the duration needed to obtain the desired impregnation degree. The duration is a function of the composition of the solvent and metallic salt in the composition, temperature of the impregnation, and desired location of the deposit of metallic aggregates.

Said duration is generally in the range from a few minutes to 20 hours.

The solution is preferably de-aired before the radiolytic reduction.

The radiolytic yield can be increased by adding a transducer of radicals (OH , H ...) into the solution. This transducer is preferably a formate of alkaline metal, a formate of ammonium, or an alcohol.

The membrane immersed in the solution of metallic ions, or the solution of metallic ions and fluoropolymer with the aim to prepare the composition of the invention in its colloidal form are then exposed to ion radiation so as to cause a radiolytic reduction of the metallic ions.

EP 0 309 337 A1

The radiation employed for the irradiation can be gamma-rays, x-rays or accelerated particles (electrons...). The irradiation can be performed at any temperature ranging between the fusion and boiling points of the solvent, if the temperature does not exceed the point of decomposition of the membrane. It can be the ambient temperature regardless of the metal or metals to be reduced. It is preferably the ambient temperature.

The applied dose of irradiation is a function of the concentration and nature of the metallic ions to be reduced, nature of the solvent, and desired metal charge.

The size and/or number of the aggregates increase with the dose of ion radiation.

With active membranes, from the beginning and to the end of irradiation, pH of the solution can be measured and adjusted so as to control the penetration of the metallic ions into the membrane.

A membrane, which has been impregnated with metallic ions by immersion in a solution, can also be put in another solution that only contains the solvent and not any metallic ions, and the assembly is then exposed to ion radiation as previously.

Advantageously, the solvent is a water/alcohol mixture; pH can be adjusted so as to cause a localized precipitation of the metallic ions in the membrane (in the form of hydroxide for example), and to thus preclude their subsequent displacement in the membrane. Said precipitation can also be achieved by adding a suitable counter-ion (Cl^- ...).

This variant provides for the acquisition of aggregates that are uniformly distributed in the entire resin of the membrane. The diameter of the aggregates are then controlled by the bulging and dose of irradiation.

After the radiolytic reduction the membrane is rinsed in distilled water and dried. It is preferably dried in an inert atmosphere, or in a primary vacuum in a desiccator.

It is also possible to prepare a composition according to the invention that is in the colloidal form, by dissolving one or several compositions according to the invention that are in the solid form, for instance a membrane containing metallic or multimetallic aggregates.

Advantageously, this takes place under inert atmosphere during the dissolution.

It is possible to use any solvent of ion exchanger fluoropolymers, advantageously solvents such as dimethylformamide or water-alcohol mixtures.

It is therefore possible to obtain colloidal solutions of metallic or multimetallic aggregates and ion exchanger fluoropolymer in two different ways, by reduction of metallic salts contained in a solution of metallic salts and fluoropolymers or by dissolution of a composition comprising a fluoropolymer and metallic aggregates.

The colloidal solutions obtained by one of the two described methods can be arrayed and dried on ion exchanger membranes.

EP 0 309 337 A1

The drying of the colloidal solution can be performed at any temperature and under reduced pressure if so desired. The temperature is delimited by the decomposition temperature for the polymer.

Adherence may be improved by heat treatment, under pressure if so desired.

This last-mentioned process can be repeated several times in the purpose of achieving stacking of polymer layers enclosing aggregates of different metals in each of the layers. Two layers each containing the same metal or a different metal can also be applied on the opposite faces of one and the same membrane. If the colloidal solution contains several metals or several alloys, it is possible to obtain membranes dressed [coated? (T.R.)] in all combinations of possible layers, each layer containing the whole combination of metals or alloys.

The same process also applies to layers containing multimetallic aggregates.

The process described in the invention allows for the generation of metallic or multimetallic aggregates, at ambient temperature, in the resin or at the surface of the ion exchanger fluoropolymers.

These aggregates are generated by radiolytic reduction of metallic salts dissolved in an appropriate solvent and are impregnated in the polymer or adsorbed at its surface. Said aggregates are constituted of a metal or a mixture of metals with the exclusion of any impurities such as boron or phosphorus present in the metallic aggregates generated by chemical processes using reduction compounds such as boron hydrides or hypophosphites.

The process according to the invention allows for the generation of metallic aggregates in the resin of a ion exchanger membrane; the localization (from the surface to the center of the membrane), the quantity of metal incorporated, and the size distribution of aggregates are controlled by the different parameters of the process.

This process also allows for the generation of an adherent deposit of metallic aggregates to the surface of an ion exchanger membrane. This surface deposit is a conductor of electricity when the charge is sufficient.

Said process also allows for the simultaneous implementation of incorporation in the resin [mass; T.R.] of the membrane, and deposit of metallic aggregates at the surface.

A variant of the process may lead to interesting applications: the fluoropolymer incorporating the metallic aggregates may be dissolved in a suitable solvent (DMF...) to obtain a colloidal solution of the metal or the metallic alloy.

This colloidal solution may also be obtained by irradiation of a solution mixed of fluoropolymer and metallic salt in a suitable solvent.

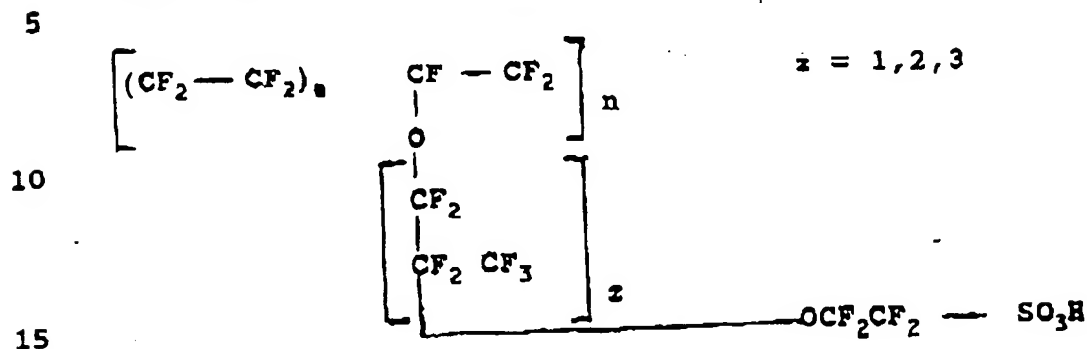
In these two cases the polymer in solution acts as surfactant.

The following examples illustrate the invention.

EP 0 309 337 A1

EXAMPLE 1

A membrane of NAFION 117 (trade mark of DU PONT DE NEMOURS and denoting a fluoropolymer of this kind:)



(chemical equivalent weight = 1100 g/mole of SO_3H , thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is then immersed for 70 hours at 20°C in a solution A containing the complex $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ at 10-2 moles/liter with, for solvent, a water/ethanol mixture (70:30% by volume) of dissolved ammonia.

The membrane is then irradiated by gamma-rays of cobalt 60, during 20 hours, in the solution A that has been previously deaired by spraying with nitrogen. The dosing rate and the dose of irradiation are 0.3 Mrad/hour and 6 Mrad, respectively.

The membrane is then rinsed in distilled water and dried under a stream of nitrogen. It has the characteristic brown color of platinum nanoaggregates.

The average total charge of platinum in the membrane is 0.3% by weight.

The micrographies obtained through electronic transmission microscopy, of sections of the membrane having approximately 50 nm thickness, show on the one hand a small superficial deposit (20 nm), and on the other hand that the diameter D of the incorporated aggregates varies as a function of the depth P in the membrane. The distribution is the following:

$0 < P < 1 \mu\text{m}$	$3 < D < 25 \text{ nm}$
$1 < P < 3 \mu\text{m}$	$1.5 < D < 10 \text{ nm}$
$3 < P < 5 \mu\text{m}$	$0.6 < D < 4 \text{ nm}$
$P < 5 \mu\text{m}$	$0.6 < D < 1,5 \text{ nm}$

60% of the total platinum charge is between the membrane surface and 1 μm of depth.

EP 0 309 337 A1

EXAMPLE 2

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is then immersed for 6 hours at 20°C in a solution containing the complex $(\text{Ir}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$ at 10^{-2} moles/liter with, for solvent, a water/ethanol mixture (90:10% by volume) of dissolved ammonia.

The membrane is then irradiated by gamma-rays of cobalt 60, during 84 hours, in a de-aired water/ethanol mixture (99:0.1%). The dosing rate and the dose of irradiation are 0.6 Mrad/hour and 50.4 Mrad, respectively.

The membrane is then rinsed in distilled water and dried under a stream of nitrogen. It has the characteristic brown color of iridium nanoaggregates.

The iridium aggregates are uniformly dispersed in the membrane. Their diameter varies between 0.6 and 2 nm. Among them 60 percent have a diameter between 0.8 and 1.5 nm.

The average iridium charge is 1% by weight.

EXAMPLE 3

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

The membrane is then exchanged in the form of Na^+ in a solution of NaOH @ 20 g/l during 16 hours and then rinsed with distilled water.

It is immersed for 15 hours in a solution containing CuSO_4 @ 5×10^{-2} moles/liter and PdCl_2 @ 5×10^{-3} moles/liter with, for solvent, a water/isopropanol mixture (90:10% by volume).

It is then irradiated for 29 hours by gamma-rays of cobalt 60, in a de-aired water/isopropanol mixture (90:10% by volume).

The dosing rate and the dose of irradiation are 0.6 Mrad/hour and 17.4 Mrad, respectively.

The membrane is then rinsed with distilled water and dried in a stream of nitrogen. It has a green brown color.

The micrographies show that the aggregates are distributed in the entire resin of the membrane. Among them 60% have a diameter between 4 and 7 nm.

The electronic diffraction performed over sections of the membrane of approx. 50 nm thickness shows that the aggregates have a structure CFC, the mesh [ring? chain? link (T.R.)] parameters of which are those of solid solutions of the two metals. Certain diffractograms show supplementary rings corresponding to the defined compounds Cu_3Pd and CuPd .

EP 0 309 337 A1

EXAMPLE 4

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

The membrane is air-dried, then immersed and irradiated for 14 hours by means of gamma-rays of cobalt 60, in a solution de-aired by means of nitrogen and containing H_2PtCl_6 @ 10^{-2} moles/liter with, for solvent, the water/ethanol mixture (70:30% by volume). pH has been previously adjusted to 6.5 with sodium.

The dosing rate and the dose of irradiation are 0.25 Mrad/hour and 3.5 Mrad, respectively.

Upon drying the membrane has a metallic reflection. The micrographies show that the deposit is localized mainly at the surface across a thickness of 0.12 μm . This deposit is constituted of aggregates whose diameters range between 1 and 5 nm. The average charge at the surface is 6.2 mg per cm^2 of membrane.

Aggregates having a diameter between 0.6 and 2 nm are distributed in the resin of the membrane with a content of 0.03% by weight.

EXAMPLE 5

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/isopropanol mixture (60:40% by volume) until the brown coloration has disappeared. It is once again rinsed with distilled water.

The membrane is then immersed for 20 hours in an aqueous solution of Ag_2SO_4 @ 10^{-3} moles/liter, pH = 6.

It is thereafter irradiated for 1 hour 15 minutes by gamma-rays of cobalt 60 in a water/isopropanol mixture (80:20% by volume) at pH = 6.8.

The dosing rate and the dose of irradiation are 0.54 Mrad/hour and 0.7 Mrad, respectively.

The membrane is rinsed with distilled water and dried with nitrogen. It has the characteristic yellow color of silver nanoaggregates.

The aggregates are uniformly distributed in the resin of the membrane with a portion of 0.04% by weight. The diameter of the aggregates varies between 0.8 and 10 nm. Among them 70% have a diameter between 4 and 6 nm.

EXAMPLE 6

102 mg (3 cm^2) of the metallized membrane in Example 5 are cut up in squares of 1 mm^2 and dissolved in 2 ml of DMF at 60°C . The colloidal solution of silver aggregates thus obtained is dried at 110°C on the sulfonic face of a membrane of NAFION 902 (20 cm^2).

EP 0 309 337 A1

The composite layer NAFION 117/silver aggregates thus obtained has a thickness of approx. 25 μm with a silver content of 0.04% by weight.

5 EXAMPLE 7

10 A solution containing 4.3% by weight of dissolved NAFION 117 and H_2PtCl_6 @ 5×10^{-4} moles/liter is prepared, with a water/ethanol mixture (99.9:0.1% by volume) as solvent. This solution is de-aired with nitrogen, then irradiated for 2 hours by gamma-rays of cobalt 60.

The dosing rate and the dose of irradiation are 0.25 Mrad/hour and 0.5 Mrad, respectively.

15 A brown colloidal solution of platinum aggregates is obtained having a diameter between 0.6 and 3 nm. 65% among them have a diameter between 1 and 2 nm.

A 2.5 ml sample of this solution is taken and dried on a (10 cm^2) NAFION 117 membrane. The layer obtained has a thickness of approx. 50 μm and contains 0.23% platinum by weight.

20 EXAMPLE 8

25 A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degassed to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

30 It is dried, then immersed for 22 hours at 25°C in a solution I containing NiSO_4 @ 10^{-1} moles/liter, HCOONH_4 @ 5×10^{-1} moles/liter and 1.2% by weight of dissolved ammonia, with a water/ethanol mixture (90:10% by volume) as solvent. The solution pH is 9.9.

The membrane is then irradiated for 40 hours by gamma-rays of cobalt 60 in the solution I that has been previously de-aired by spraying with nitrogen.

35 The dosing rate and the dose of irradiation are 0.61 Mrad/hour and 24.4 Mrad, respectively.

The membrane is then rinsed with distilled water and dried in a stream of nitrogen. It has a metallic reflection.

40 The micrographies obtained through electronic transmission microscopy, and taken of sections of the membrane having approximately 50 nm thickness, show on the one hand a small superficial deposit of 0.13 μm thickness constituted by metallic aggregates of a 3 - 10 nm diameter, and on the other hand the presence of nickel aggregates of a 3.8 ± 2 nm diameter down to an 8 μm depth from the membrane surface.

45 The deposit at the surface conducts electricity. The average charge at the surface is 2.5 mg per cm^2 of membrane.

EP 0 309 337 A1

EXAMPLE 9

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is dried and then immersed for 22 hours at 25°C in a solution II containing NiSO_4 @ 10^{-1} mole/liter and HCOONa @ 5×10^{-1} mole/liter with a water/ethanol mixture (70:30% by volume) as solvent. The pH-value of the solution II, initially being 6.8, diminishes to 5.6 by the end of the impregnation.

The membrane is then irradiated for 40 hours by gamma-rays of cobalt 60 in the solution II previously de-aired by way of spraying with nitrogen. The dosing rate and the dose of irradiation are 0.61 Mrad/hour and 24.4 Mrad, respectively.

It is rinsed with distilled water and then dried under 10^{-2} Torr in a desiccator.

The membrane has a very intense brown color characteristic of metal nanoaggregates such as nickel.

The micrographies obtained through electronic transmission microscopy show that the aggregates of nickel are dispersed across a depth of 15 μm in the resin of the membrane and that 70% among them have an average diameter of 23 ± 5 nm.

The average charge by weight of nickel in the membrane is 0.05.

EXAMPLE 10

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μm) is degreased to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is dried and then immersed for 4 hours at 80°C in a solution III containing NiSO_4 @ 5×10^{-1} mole/liter and HCOONa @ 5×10^{-2} moles/liter with a water/ethanol mixture (80:20% by volume) as a solvent.

It is then dried and immersed for 10 minutes in a solution III containing HCOONa @ 1 mole/liter with a water/ethanol mixture (90:10% by volume) as a solvent. The pH of the solution III has been previously adjusted to 11.5 with a concentrated solution of NaOH.

The membrane is once again dried and analyzed with a spectrophotometer UV-VIS to control the precipitation of $\text{Ni}(\text{OH})_2$ in the resin of the polymer.

It is then irradiated for 34 hours by gamma-rays of cobalt 60 in the solution III previously de-aired with nitrogen. The dosing rate and the dose of irradiation are 0.3 Mrad/hour and 10.2 Mrad, respectively. The membrane is then rinsed with distilled water and dried under nitrogen.

EP 0 309 337 A1

It has the brown characteristic color of nanoaggregates of metals such as nickel.

The micrographies show that the aggregates of nickel are uniformly dispersed in the resin of the membrane and that they have an average diameter of 3 ± 1.5 nm.

The charge by weight of nickel in the membrane is 0.01%.

EXAMPLE 11

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μ m) is degassed to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is dried and then immersed for 5 hours at 50°C in a solution IV containing NiSO_4 @ 2×10^{-1} mole/liter, CuSO_4 @ 10^{-1} mole/liter and HCOONa @ 10^{-2} moles/liter with a water/ethanol mixture (80:20% by volume) as a solvent.

The membrane is then dried and immersed for 10 minutes in a solution IV containing HCOONa @ 10 moles/liter with a water/ethanol mixture (60:40% by volume) as a solvent. The pH of the solution IV has been previously adjusted to 12.1 with a concentrated solution of NaOH.

The membrane is once again dried and analyzed with a spectrophotometer UV-VIS to control the precipitation of $\text{Ni}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ in the resin of the polymer.

It is then irradiated for 63 hours by gamma-rays of cobalt 60 in the solution IV previously de-aired with nitrogen. The dosing rate and the dose of irradiation are 0.61 Mrad/hour and 38.4 Mrad, respectively. The membrane is then rinsed with distilled water and dried under nitrogen. It has a dark red color.

The micrographies show that the aggregates are uniformly dispersed in the resin of the membrane and that they have an average diameter of 6 ± 2.5 nm.

The electronic diffraction shows that the aggregates have a structure CFC with a mesh parameter equal to 0.357 ± 0.003 nm (3.57 ± 0.03 Å [Angstrom units]) which corresponds to solid nickel/copper solutions of 20% - 80% by copper atoms.

The charges by metallic weight of copper and nickel are 0.054% and 0.043%, respectively.

EXAMPLE 12

A membrane of NAFION 117 (chemical equivalent weight = 1100, thickness = 180 μ m) is degassed to F113, then boiled in a water/ethanol mixture (70:30% by volume) until the brown coloration has disappeared.

It is dried and then immersed for 2 hours at 25°C in a solution V containing NiSO_4 @ 5×10^{-2} moles/liter, CuSO_4 @ 10^{-1} mole/liter and HCOONa @ 10^{-2} moles/liter with a water/ethanol mixture (80:20% by volume) as a solvent.

EP O 309 337 A1

The membrane is then dried and immersed for 10 minutes in a solution V containing HCOONa @ 5×10^{-1} mole/liter with a water/ethanol mixture (85:15% by volume) as a solvent. The pH of the solution V has been previously adjusted to 11.8 with a concentrated solution of NaOH .

The membrane is once again dried and analyzed with a spectrophotometer UV-VIS to control the precipitation of $\text{Ni}(\text{OH})_2$ and $\text{Cu}(\text{OH})_2$ in the resin of the polymer.

It is then irradiated for 15 hours by gamma-rays of cobalt 60 in the solution V previously de-aired with nitrogen. The dosing rate and the dose of irradiation are 0.3 Mrad/hour and 4.5 Mrad, respectively.

The membrane is then rinsed with distilled water and dried under nitrogen. It has a brown color characteristic of nanoaggregates of these two metals.

The micrographies show that the aggregates are uniformly dispersed in the membrane and that they have an average diameter of 3.7 ± 1.7 nm.

The charges by metallic weight of cobalt and nickel are 0.002 and 0.003%, respectively.

EXAMPLE 13

A solution VI containing 0.84% by weight of dissolved NAFION 117, $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ @ 1.2×10^{-3} moles/liter and HCOONa @ 1.9×10^{-2} moles/liter with, for solvent, a water/ethanol mixture (86:14% by volume) is prepared.

The solution VI is de-aired by spraying with nitrogen and then irradiated for 17 hours by gamma-rays of cobalt 60. The dosing rate and the dose of irradiation are 0.33 Mrad/hour and 5.6 Mrad, respectively.

The result is a subcolloidal solution of brown, yellow color containing 2.9% of the weight of the polymer as metallic lead.

A drop of this solution diluted 20 times is dried on a rack and examined by means of electronic transmission microscopy. The observed lead aggregates have a diameter of 2 ± 0.5 nm.

A 5 ml sample of the non-diluted colloidal solution is taken and dried on the composite layer of NAFION 117/Pt-aggregates of Example 7. The second layer obtained has a thickness of approx. 20 μm and contains 2.9% lead by weight.

EXAMPLE 14

A solution VII containing 4.5% by weight of dissolved NAFION 117 and CuSO_4 @ 4.5×10^{-4} moles l^{-1} [per liter? (T.R.)] with a water/isopropanol mixture (98:2% by volume) as a solvent is prepared.

A solution VIII containing 4.5% by weight of dissolved NAFION 117 and Ag_2SO_4 @ 2.4×10^{-4} moles l^{-1} with a water/isopropanol mixture (98:2% by volume) as a solvent is prepared.

EP 0 309 337 A1

The solutions VII and VIII are de-aired by spraying with nitrogen and then irradiated for 54 minutes by gamma-rays of cobalt 60. The dosing rates and the doses of irradiation are 0.95 Mrad/hour and 0.86 Mrad, respectively, for solution VII, and 0.20 Mrad/hour and 0.18 Mrad, respectively, for solution VIII. Two colloidal solutions are obtained:

The colloidal copper solution of red color contains 0.063% by weight of metallic polymer of copper. The aggregates have an average diameter of 9.2 nm.

The colloidal silver solution of yellow color contains 0.11% by weight of metallic polymer of silver. The aggregates have an average diameter of 4.5 nm.

0.4 ml of the colloidal silver solution and 3 ml of the colloidal copper solution are mixed under nitrogen. The result is a colloidal solution containing respectively 0.056% copper and 0.013% silver by weight of the metallic polymer.

P a t e n t C l a i m s :

1. A composition comprising metallic or multimetallic aggregates and at least one ion exchanger fluoropolymer.

2. A composition as claimed in Claim 1, characterized in that the aggregates have an average diameter smaller than 50 nm and are composed of one or several metals selected among noble and non-noble metals.

3. A composition as claimed in either one of Claims 1 and 2, characterized in that the aggregates are a mixture of aggregates of a metal 1 and of aggregates of a metal 2, wherein metal 1 and metal 2 each can be a mixture of one or several metals selected among noble and non-noble metals.

4. A composition as claimed in any one of Claims 1 - 3, characterized in that the composition is in a colloidal form.

5. A composition as claimed in any one of Claims 1 - 3, characterized in that the ion exchanger fluoropolymer is in the form of a membrane.

6. A composition as claimed in Claim 5, characterized in that the aggregates are distributed in the resin of the membrane.

7. A composition as claimed in Claim 6, characterized in that the diameter of the aggregates varies according to their localization depthwise.

EP 0 309 337 A1

8. A composition as claimed in Claim 5, characterized in that the aggregates are distributed at the surface of the membrane.

9. A composition as claimed in Claim 5, characterized in that the aggregates are distributed at the surface and in the resin of the membrane.

10. A process for preparing said composition according to any one of Claims 1 - 5, characterized in that a solution of at least one metallic salt is brought into contact with the ion exchanger fluoropolymer, and, then, by implementing a radiolytic reduction of the metallic salt or salts.

11. A process as claimed in Claim 10, characterized in that the solvent of the solution of metallic salts is a water/alcohol mixture.

12. A process for preparing said composition as claimed in Claim 1, characterized by dissolving, in a solvent, one or several compositions comprising metallic or multimetallic aggregates and at least one ion exchanger fluoropolymer.

13. A process for preparing said composition as claimed in either one of Claims 8 and 9, characterized by depositing, on the membrane, a colloidal solution as claimed in Claim 4, and then implementation of drying followed, if necessary, by thermal treatment.

14. A process as claimed in Claim 13, characterized in that the metal or metals of the aggregates of the colloidal solution are different from the metal or metals of the aggregates that are possibly contained in the membrane.

15. A process as claimed in either one of Claims 13 and 14, characterized by depositing one or several layers of polymers on each face of the membrane, the metal or metals of the aggregates in each layer having the possibility of being different.

ogo)
European Patent Office

EUROPEAN SEARCH REPORT

Application No. EP 88 40 2371

DOCUMENTS CONSIDERED AS PERTINENT

Category	Citation of the document with indication, if necessary, of pertinent portions thereof	Claims concerned	Classification of the application (Int. Cl.)
----------	---	------------------	--

JOURNAL OF ELECTROANAL. CHEM. vol. 158, no. 1, 1983, pages 181-185, Elsevier Sequoia S.A.; "H-Y. LIU et al.: "Redox mediation of dioxygen reduction within nafion electrode coatings containing platinum as catalyst"
Experimental

1,2

C 08 K 3/08
C 08 L 27/12
C 08 J 5/22

A EP-A-0 165 177 (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE)

JOURNAL OF PHYS. CHEM., vol. 90, 1986, pages 6353-6358, American Chemical Society; M.G. ALONSO-AMIGO et al.: "Detection of isolated and paired Cu²⁺ ions in nafion membranes by ESR spectroscopy"

TECHNICAL
SEARCH FIELDS
(Int. Cl.)

C 08 K
C 08 L
C 08 J

The present report has been established for all of the claims.

Place of Search
The Hague, Holland

Date of Search
Dec. 18, 1988

Search Examiner
DE LOS ARCOS Y VELAZQUES

CATEGORY OF CITED DOCUMENTS

particularly pertinent if taken alone

cited in the application